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by

A. N. Mansour and C. A. Melendres

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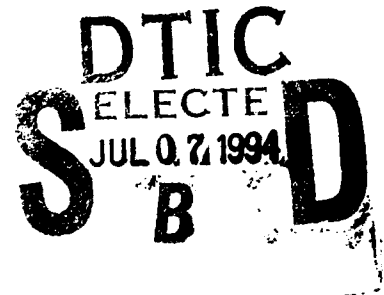
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# X-ray Absorption Spectra and Structure of Some Nickel Oxides (Hydroxides)

A. N. Mansour\* and C. A. Melendres<sup>+</sup>

\*Naval Surface Warfare Center, Silver Spring, MD 20903-5000

<sup>+</sup>Argonne National Laboratory, Argonne, IL 60439

## Introduction:

The structure of the higher oxide forms of nickel (where Ni has a valency greater than +2) is of great interest from the standpoint of developing advanced nickel batteries for consumer applications and for electric vehicle propulsion. In spite of various research efforts, much uncertainty and confusion still exists with regard to the stoichiometry and structure of the various oxides (hydroxides) that are formed during the charging (and discharging) of the nickel electrode.<sup>1</sup> The difficulty stems in part from the highly disordered or amorphous nature of the phases formed which makes structural determination by X-ray diffraction difficult. X-ray absorption fine structure (XAFS) spectroscopy is an excellent technique for the characterization of such materials which have no long range order and can be used for in situ measurements.<sup>2-4</sup> Preliminary to using XAFS spectroscopy for "in-situ" structural determinations in an electrochemical cell, we have used it to study a number of standard samples for subsequent use as reference for electrochemically prepared (ECP) phases. Recently, we have investigated the Ni valency and local atomic structure in chemically prepared (CP)  $\beta$ -NiOOH,  $\text{Ni}_3\text{O}_2(\text{OH})_4$ ,  $\text{NiO}_2$  and  $\text{KNiIO}_6$  and published the first XAFS spectrum of quadrivalent Ni.<sup>5,6</sup> In the present investigation we report the results of an XAFS study on the Ni valency and local atomic structure in  $\alpha$ -Ni(OH)<sub>2</sub>,  $\text{Ni}_2\text{O}_3$ , CP and ECP  $\gamma$ -NiOOH.

## Experimental:

The  $\alpha$ -Ni(OH)<sub>2</sub> and  $\text{Ni}_2\text{O}_3$  samples were prepared following the procedures outlined by Hutting et al.<sup>7</sup> and Cairns et al.<sup>8</sup>, respectively. The CP  $\gamma$ -NiOOH sample was synthesized by the chemical oxidation of  $\text{Ni}(\text{NO}_3)_2$  with  $\text{K}_2\text{S}_2\text{O}_8$ .<sup>9</sup> The ECP  $\gamma$ -NiOOH sample was synthesized by the anodic oxidation of anodically formed  $\alpha$ -Ni(OH)<sub>2</sub>.<sup>10</sup> All samples were examined initially by powder X-ray diffraction (XRD) for preliminary phase identification. XAFS spectra were measured on beamline X11A of the National Synchrotron Light Source (NSLS). XAFS spectra around the Ni K-edge (8333 eV) were measured in transmission

with the storage ring operating at 2.52 GeV beam energy and beam currents in the range of 110-220 mA. The spectrum of a 6  $\mu\text{m}$  thick Ni foil was measured simultaneously for use as reference in calibrating the energy scale.

### Results and Discussion:

Figure 1 shows room temperature XANES spectra of  $\alpha\text{-Ni(OH)}_2$ ,  $\text{Ni}_2\text{O}_3$ , CP and ECP  $\gamma\text{-NiOOH}$  along with those of Ni foil and  $\text{KNiIO}_6$  being used for comparison purposes. Figure 2 shows the pre-edge region extending from 8323 to 8337 eV which displays the contribution due to the transition from the 1s core level to unoccupied bound d-states. The weak intensity associated with this transition is due to the fact that this transition is forbidden by dipole selection rules. It is allowed by quadrupole selection rules or as a result of hybridization between states with p and d characters. The Ni K-edge energies for both the main edge and the pre-edge peak are listed in Table I. As expected, the Ni K-edge energy shifts to higher energies as the oxidation state increases from  $\text{Ni}^0$  (metallic Ni) to  $\text{Ni}^{+2}$  ( $\alpha\text{-Ni(OH)}_2$ ) to  $\text{Ni}^{+4}$  ( $\text{KNiIO}_6$ ). The latter is among the few compounds where Ni has been fairly well established to be in the quadrivalent state.<sup>8</sup> The observed shifts suggest that the average valency of Ni in the compounds investigated increases in the order  $\alpha\text{-Ni(OH)}_2$ ,  $\text{Ni}_2\text{O}_3$ , ECP  $\gamma\text{-NiOOH}$ , CP  $\gamma\text{-NiOOH}$ , and  $\text{KNiIO}_6$ .

Figure 3 shows a comparison of Fourier transforms of  $k^3$ -weighted EXAFS spectra for  $\alpha\text{-Ni(OH)}_2$ ,  $\text{Ni}_2\text{O}_3$ , CP and ECP  $\gamma\text{-NiOOH}$  performed over the photoelectron wave number,  $k$ , range of approximately 2.6 and 16.1  $\text{\AA}^{-1}$ . The first shell of atoms, in the range of 1 to 2  $\text{\AA}$ , corresponds to oxygen octahedrally coordinating the Ni atoms. The second shell of atoms, in the range of 2 to 3  $\text{\AA}$ , corresponds to Ni-Ni interactions in the hexagonal planes. The first and second shells of atoms were filtered, backtransformed to  $k$ -space and quantitatively analyzed using non-linear least square fitting methods. Based on the brucite structure, the sum of the coordination numbers for each of the Ni-O and Ni-Ni interactions was constrained to equal 6 atoms. In addition, we assumed that all atoms within a specific shell have the same disorder. A summary of EXAFS results are listed in Table II. They indicate that the fraction of  $\text{Ni}^{+4}$  (i.e., Ni with short distance) increases from 40% in  $\text{Ni}_2\text{O}_3$  to 70% in ECP  $\gamma\text{-NiOOH}$  to 80% in CP  $\gamma\text{-NiOOH}$ .

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TABLE I. Summary of Ni K-edge energies.

Compound	Ni K-edge energy <sup>1</sup>	Ni K-edge energy <sup>2</sup>
Ni	8336.9	N/A
$\alpha$ -Ni(OH) <sub>2</sub>	8338.1	8328.2
Ni <sub>2</sub> O <sub>3</sub>	8339.6	8328.7
$\gamma$ -NiOOH (CP)	8341.2	8329.7
$\gamma$ -NiOOH (ECP)	8340.3	8329.2
KNiO <sub>6</sub>	8343.0	8330.6

<sup>1</sup>Ni K-edge energy measured as the energy at which the normalized absorption ( $\mu x$ ) is equal to 0.5.

<sup>2</sup>Ni K-edge energy measured as the energy of the inflection point at the onset of the 1s to 3d transition.

Table II. Summary of Ni local structure parameters as determined from XAFS spectra using theoretical standards generated with the FEFF code.

Compound	X-Y Pair	N	R (Å)	$\sigma^2(10^{-3}\text{\AA}^2)$
Ni	Ni-Ni	12.0	2.480(2.492)	5.5
NiO	Ni-O	6.0	2.079(2.089)	4.5
	Ni-Ni	12.0	2.946(2.954)	5.5
$\alpha$ -Ni(OH) <sub>2</sub>	Ni-O(1)	1.0	1.90	3.7
	Ni-O(2)	5.0	2.05	3.7
	Ni-Ni(1)	0.4	2.85	8.3
	Ni-Ni(2)	5.6	3.12	8.3
Ni <sub>2</sub> O <sub>3</sub>	Ni-O(1)	2.2	1.87	7.8
	Ni-O(2)	3.8	2.03	7.8
	Ni-Ni(1)	2.5	2.88	8.1
	Ni-Ni(2)	3.5	3.07	8.1
$\gamma$ -NiOOH (CP)	Ni-O(1)	4.6	1.89	5.1
	Ni-O(2)	1.4	2.12	5.1
	Ni-Ni(1)	4.7	2.84	4.2
	Ni-Ni(2)	1.3	3.08	4.2
$\gamma$ -NiOOH (ECP)	Ni-O(1)	4.0	1.89	7.0
	Ni-O(2)	2.0	2.08	7.0
	Ni-O(1)	3.9	2.84	6.4
	Ni-O(2)	2.1	3.07	6.4
KNiIO <sub>6</sub>	Ni-O	6.0	1.88	3.5

N: coordination number,

R: bond distance (Distances in parentheses correspond to the well known crystallographic distances).

$\sigma^2$ : mean square displacement

Figure Captions:

Figure 1 Ni K-edge XANES.

Figure 2 Ni K-edge pre-edge region (i.e, 1s to 3d transition).

Figure 3 Fourier transforms of Ni K-edge EXAFS ( $k^3$ -weighted).  
The data for  $\text{Ni}_2\text{O}_3$ , chemically prepared (CP) and  
electrochemically prepared (ECP)  $\gamma$ -NiOOH has been  
shifted vertically for clarity of presentation.

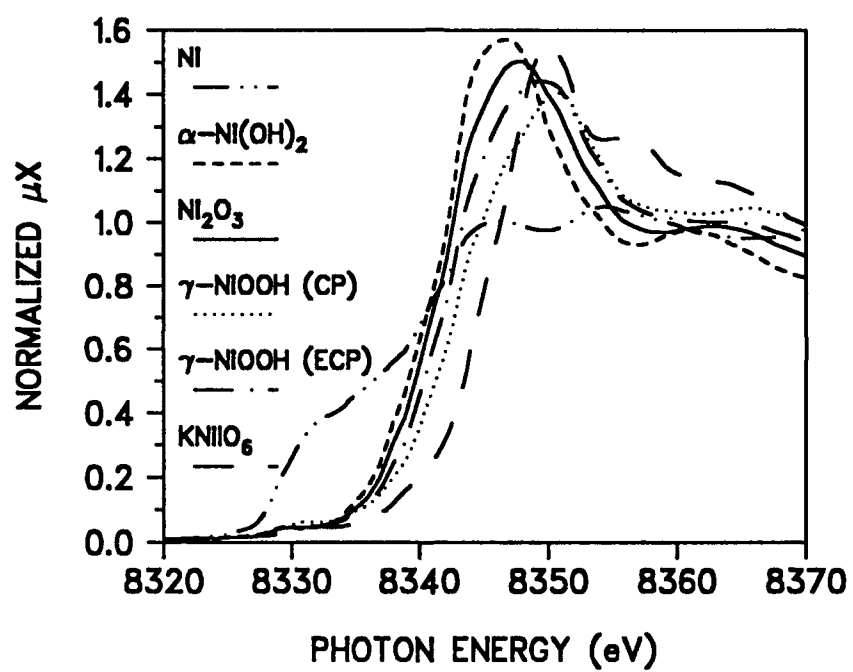


Fig. 1



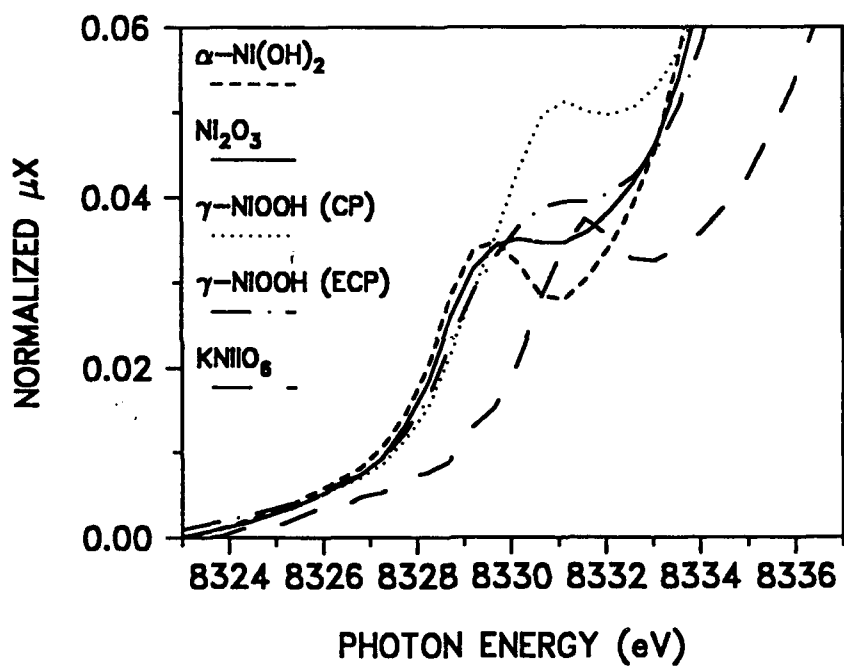


Fig. 2

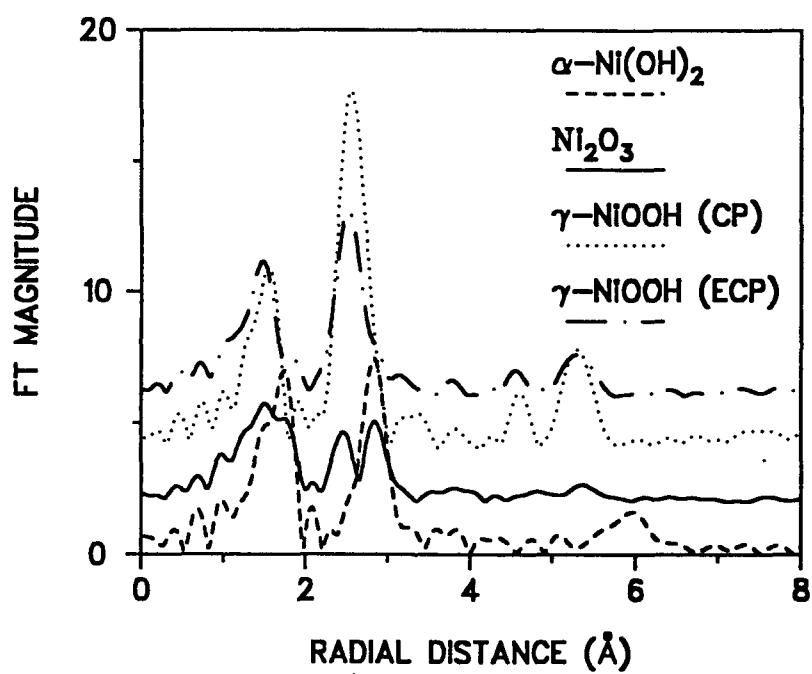


Fig. 3